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基于嵌段共聚物构筑微/纳米有序多孔材料

Micro/Nanoporous Materials from Block Copolymer Precursors

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摘 要

有序多孔材料在催化、传感、吸附与分离等方面具有重要的应用前景，其制备历来是研究者们关注的热点领域。嵌段共聚物具有特殊的物理化学性质和独特的自组装性能，是一种构筑微/纳米有序多孔材料的理想前驱体。人们一般利用嵌段共聚物微相分离模板法(最近在此技术上发展了一种聚合物双连续微乳液法)来制备结构有序的多孔材料，通常做法是：将嵌段共聚物(或嵌段共聚物与相应均聚物的共混物)浇铸成膜或块体材料，进行退火处理形成球状、柱状或双连续立方状等平衡相结构，利用物理或化学方法选择性去除其中一相后得到孔径介于5-100 nm之间的有序多孔材料。这种方法的优点是人们可以根据嵌段共聚物(或共混物)的组成借助理论对所形成的平衡相结构进行预测，或是根据所需要的平衡相结构对体系的组成进行设计，最后获得相应类型的孔结构。但该方法必须先对体系进行足够时间的退火处理，达到平衡态后才能利用臭氧、UV、高温等手段选择性去除其中一组分来进行孔结构的构筑。成孔过程中产生的结构缺陷和难以去除干净的残留物等会在一定程度上限制此类技术在微电子工业和生物材料等方面的进一步应用和发展。因此，采用非破坏性的方法来制备有序多孔材料无论是在学术上还是实际应用中都具有极其重要的价值和意义。

呼吸图法(又称水滴模板法)是一种简单有效、不需要去除模板的制备有序多孔结构的自组装技术。超临界流体选择溶胀法则是新近发展起来的一种可以在非平衡态体系下构筑纳米有序多孔材料的技术，具有非破坏性的特点。本文以聚苯乙烯-*b*-聚丙烯酸(PS-PAA)、聚苯乙烯-*b*-聚 2-(全氟辛基)乙基甲基丙烯酸酯(PS-PFMA)、聚苯乙烯-*b*-聚二甲基硅氧烷(PS-PDMS)和聚苯乙烯-*b*-聚(4-乙烯基吡啶) (PS-P4VP)等嵌段共聚物作为前驱体，结合这两种技术，成功制备了孔径尺寸在50 nm-5 μm之间多种类型的有序多孔材料。

我们首先利用原子转移自由基聚合(ATRP)技术合成了分子量分布在 1.1 以下的两亲性嵌段共聚物 PS-PAA 和含氟嵌段共聚物 PS-PFMA。然后以 PS-PAA 作为铸膜材料，利用静态呼吸图技术，在透射电镜(TEM)铜网、糖颗粒和图案化硅片等非平面上成功制备了三维有序多孔薄膜。铸膜溶剂对聚合物的塑化效应和

高度规整的蜂窝状有序结构是高玻璃化转变温度的PS-PAA薄膜能够良好复制非平面基底表面形貌而不会产生应力开裂的主要原因。利用 PS-PAA 和二茂铁(Cp_2Fe)的混合溶液在 TEM 铜网上浇铸成膜，制备了具有催化活性的三维有序多孔杂化膜。去除铜网后得到了多级有序的蜂窝状多孔杂化膜。通过 UV 交联，有效地提高了杂化多孔膜的热稳定性；进一步热处理则使 Cp_2Fe 在 PS-PAA 结构导向剂的作用下原位分解并氧化形成多级有序的 Fe_2O_3 图案。采用交联后的有序杂化膜和 Fe_2O_3 图案作为模板，经 CVD 处理后分别得到了多级有序的束状碳纳米管阵列图案和蜂窝状碳纳米管阵列图案。

以 PS-PFMA 和 PS-PDMS 等含亲 CO_2 组分的嵌段共聚物作为铸膜材料，选用不同溶剂浇铸成膜后，利用超临界流体选择溶胀技术对其进行处理，得到了有序的孔、球以及蜂窝状等纳米结构。在此基础上，发展了一种气体膨胀液体选择溶胀技术。以不含亲 CO_2 组分的 PS-P4VP 为模板，经气体膨胀甲醇或气体膨胀乙醇在温度为 45-60 ℃和压力为 12-20 MPa 等条件范围下处理后，制备得到了一系列 BET 比表面积不同的网络结构多孔 PS-P4VP。其中，60 ℃，20 MPa 条件下气体膨胀甲醇法制备的样品比表面积最高，达到 103.9 m^2/g。结合电化学和吸附-还原等技术，以网络结构多孔 PS-P4VP 作为模板，制备得到了与模板形貌结构互补的多孔聚吡咯和多孔铂。在自制的化学电阻型气体传感装置中对多孔聚吡咯进行氨气敏感性能检测，发现引入了纳米多孔结构的聚吡咯膜对氨气的敏感性能显著提高，其对应的电阻变化率(相对致密聚吡咯膜)增加了近十倍。

关键词：嵌段共聚物 有序多孔结构 超临界流体 呼吸图

Abstract

Micro/nanoporous materials have been shown to be useful for many applications including sensors, catalysis, adsorption and separation. In the case of porous materials prepared from block copolymer precursors, the self-assembly of block copolymers in particular, followed by selective removal of one block, has proven to be a fruitful route to ordered nanoporous materials. There are many removal strategies for the etchable block, including thermal treatment, UV degradation, and ozonolysis. However, strong oxidation or high temperature may limit the applicability of the process. Full degradation of a macroscopic sample can be difficult to achieve when the original structure is a discrete spherical domain structure, from which there are no paths for the decomposed fragments escaping. Such decomposed fragments may remain in the materials and cause secondary contamination. A nondestructive process without residue is more desired in both scientific and practical viewpoints. In this dissertation, two techniques, the static breath figure (BF) method and selectively swelling method, are employed to fabricate micro/nanoporous materials, using block copolymers as precursors.

The BF process is a facilely and cheaply self-assembling strategy for the fabrication of large scale patterns with an ordered 2D array of holes developed by François et al, without the need for removal of templates. Quite recently, a modified process, named static BF technology, was developed by using static saturated water vapor as the source of water droplets instead of moist airflow. Herein, with the developed BF method, the construction of macroporous polymeric films on various nonplanar substrates was studied, using a linear block copolymer with high glass transition temperature (chapter 3). Polystyrene-*b*-poly (acrylic acid) (PS-PAA), synthesized by atom transfer radical polymerization (ATRP), was employed to prepare 3-dimensional macroporous films on different nonplanar substrates, including transmission electron microscope (TEM) grid, sugar crystal and patterned Si wafer. Scanning electronic

microscopy views on the side wall in addition to views in-plane prove that polymer films with BF array perfectly replicated the surface features of these substrates. The formation processes of macropores on these substrates are analyzed in detail, and it demonstrates that neither molecular topography nor glass transition temperature of polymers is the critical factors contouring nonplanar substrate. A new hypothesis involving polymer plasticization and conformation during the solvent evaporation is formulated.

Based on the work above, a new method was developed to prepare multi-level carbon nanotube (CNT) arrays with adjustable patterns, by a combination of the static BF process and chemical vapor deposition (chapter 3). PS-PAA/ferrocene was dissolved in carbon disulfide and cast onto a Si substrate covered with a TEM grid in saturated relative humidity. A two-level microporous hybrid film with a block copolymer skeleton formed on the substrate after evaporation of the organic solvent and water. One level of ordered surface features originates from the contour of the hard templates; while the other level originates from the condensation of water droplets (BF arrays). Ultraviolet irradiation effectively cross-linked the polymer matrix and endowed the hybrid film with improved thermal stability. In the subsequent pyrolysis, the incorporated ferrocene in the hybrid film was oxidized and turned the polymer skeleton into the ferrous inorganic micropatterns. Either the cross-linked hybrid film or the ferrous inorganic micropatterns could act as a template to grow the multi-level CNT patterns, e.g. isolated and honeycomb-structured CNT bundle arrays perpendicular to the substrate.

Supercritical carbon dioxide ($scCO_2$) selectively swelling technique, introduced in 2004 by Li et al, is a unique and nondestructive methodology for the generation of nanostructured polymeric films and monoliths. In chapter 4, two kinds of block copolymers with CO_2-philic composition, Polystyrene-*b*-polydimethysiloxane (PS-PDMS, prepared by living anionic polymerization) and polystyrene-*b*-poly(perfluorooctylethyl methacrylate) (PS-PFMA, prepared by ATRP), were used for the fabrication of nanoscale structures. Firstly，thin Films of PS-PFMA were spin-cast onto silicon wafers and shown to contain PFMA

"nanodomains". Saturated in $scCO_2$ at 20 MPa and 60 ^oC, the CO_2-philic nanodomains were highly swollen and surrounded by the less swollen PS continuous matrix. The sequent isobaric quench to 0 °C was the key step to successfully fabricate nanocells in polymer thin films and monoliths. The PS matrix is frozen so that the fixed nanocellular structures are preserved during the depressurization process. Eventually, closed nanocells were formed. Here, the $scCO_2$ not only allows for expansion of the film, but also acts as a porogen of sorts. Simply changing the initial morphologies in the as-cast films (controlled by the selectivity of casting solvents), Tuning process conditions, or utilizing methanol (or hexane) as an assisted solvent, a variety of interesting nanostructures, including isolated nanocells, nanochannels, closely packed spheres and networks were fabricated after $scCO_2$ processing. Then, this methodology was extended to PS-PDMS, the PDMS domain of which is a CO_2-philic polymer, to fabricate hexagonal or finger pattern in thin films. The prepared films could be converted into ordered silica patterns on substrates by oxidation.

In chapter 5, the selectively swelling methodology was further developed by using CO_2-expanded liquid (CXL) as solvent instead of $scCO_2$. With CXLs, polymeric films with nanoscale network were prepared by selectively swelling amphiphilic diblock copolymer, polystyrene-*b*-poly (4-vinylpyridine) (PS-P4VP). The influences of temperature, solvents (methanol, ethanol and water) and saturation pressure on the network formation were investigated in detail. Both methanol and ethanol can be expanded by CO_2, forming homogeneous CXLs, which are able to produce nanostructures in PS-P4VP films, but CO_2/water mixture failed to fabricate nanostructures in PS-P4VP films because water has essentially no change in properties when it was expanded by CO_2. Using both CO_2/methanol and CO_2/ethanol systems, the network structures could be obtained in a pressure range of 12-20 MPa and temperature scope of 45-60 ^oC. Furthermore, the resulting network structured polymeric films were employed as templates, for the preparation of polypyrrole and Pt networks, by an electrochemical polymerization and an adsorption/reduction process, respectively. The prepared porous polypyrrole film

was used to fabricate a chemoresistor-type gas sensor which showed high sensitivity towards ammonia.

Key words: Block copolymer; Ordered porous structure; Supercritical fluid; Breath figure

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